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Preparation and carbonylation of ring-functionalized methyl zirconocenes [(.eta.5-C5H4)P(C6H5)2]2Zr(CH3)2-nCln (n = 0, 1). Observation and x-ray structure of a fluxional acyl-phosphonium moiety in the complex [cyclic] [(.eta.5-C5H4)P(C6H5)2][(.eta.5-C5H4)P(C6H5)2Zr[.eta.2-(OC)CH3]Cl

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entiation was readily and unambiguously made on the basis of the FT-IR spectra of compounds **10** and **12**–**14**.

Conclusions. The equatorially protonated azasilatrane cations **6** and **11**, which could not be isolated by direct protonation of **5a,b** with strong acids,[8] can be prepared by the reaction of these azasilatranes with the weakly electrophilic Me_3SiN_3 or Me_3SiNCS. The concomitant formation of N-trimethylsilylated azasilatranes indicates that formation of these cations involves free HN_3 or HSCN, liberated in situ through nucleophilic attack of N_{eq} of the azasilatrane on the silicon of the Me_3SiX reagent. The nature and the stoichiometry of the crystalline end product appears to be governed by delicate differences in crystal-packing forces. The crystal structure of **10** confirms two earlier conclusions[8] concerning the structure of cation **6**, namely that the Si–N_{eq} bond to the protonation site is significantly longer than the other two Si–N_{eq} bonds and that one of the protons at the protonation site is engaged in a hydrogen bond with the counterion. In cation **10** (and presumably in **6**), the Si–H bond points toward one of the protons at the protonation site, which could account for the ease with which hydrogen is eliminated in their thermolysis reactions to give **13** and **8**, respectively.

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Supplementary Material Available: Tables of anisotropic thermal parameters, bond lengths and bond angles, torsional angles, least-squares planes, and general displacement parameters (8 pages); a table of calculated and observed structure factors (14 pages). Ordering information is given on any current masthead page.

Preparation and Carbonylation of Ring-Functionalized Methyl Zirconocenes $[(\eta^5\text{-}C_5H_4)P(C_6H_5)_2]_2Zr(CH_3)_{2-n}Cl_n$ (n = 0, 1). Observation and X-ray Structure of a Fluxional "Acyl–Phosphonium" Moiety in the Complex $[(\eta^5\text{-}C_5H_4)P(C_6H_5)_2][(\eta^5\text{-}C_5H_4)\overline{P(C_6H_5)_2]Zr[\eta^2\text{-}(OC}){CH_3}]Cl$

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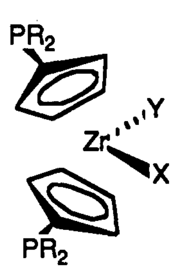
The interaction of $[(\eta^5\text{-}C_5H_4)P(C_6H_5)_2]_2ZrCl_2$ which 2 equiv of methyl Grignard reagent or methyllithium gives $[(\eta^5\text{-}C_5H_4)P(C_6H_5)_2]_2Zr(CH_3)_2$ (I), which is readily converted to $[(\eta^5\text{-}C_5H_4)P(C_6H_5)_2]_2Zr(CH_3)Cl$ (II) by treatment with $^1/_2$ equiv of lead(II) chloride. No acyl complex is observed in the reaction of these methyl zirconocenes with CO, but a product that results from attack of the ring-bound phosphine on a transient acyl complex is obtained. The complex $[(\eta^5\text{-}C_5H_4)P(C_6H_5)_2][(\eta^5\text{-}C_5H_4)\overline{P(C_6H_5)_2]Zr[\eta^2\text{-}(OC})CH_3]Cl$ (III) can be isolated from the action of CO on II, and this formulation is verified by the single-crystal X-ray study. III crystallizes from dichloromethane/diethyl ether in a monoclinic system (space group $P2_1/c$) with $Z = 4$, a = 12.3056 (12) Å, b = 18.5738 (18) Å, c = 13.5718 (15) Å, β = 101.285 (8)°, V = 3042.0 (5) Å^3, and R = 3.6% (R_w = 4.3%) for 4851 observed reflections. Variable-temperature NMR studies indicate that the carbonylation products are fluxional and undergo intramolecular attack by the phosphorus on the other cyclopentadienyl ring. An activation enthalpy of 61 kJ/mol was observed for this process with III in dichloromethane-d_2.

Introduction

This group[1,2] and others[3] have been interested in the use of phosphinocyclopentadienides as bifunctional ligands. Our work has focused on the zirconocenes $[(\eta^5\text{-}C_5H_4)PR_2]_2ZrXY$ (A) as chelating ligands for the formation of heterobinuclear complexes.



A

We have reported the preparation of such compounds A where X = Y = Cl and R = C_6H_5, CH_3 as well as their complexes with the $Mo(CO)_4$ fragment.[1,2] Our interest in these metallo ligands is that one can tune the electrophilicity and/or steric bulk of the zirconium center by changing the substituents X and Y from halide to different alkyl groups. Here we present the synthesis and characterization of methyl derivatives of $[(\eta^5\text{-}C_5H_4)P(C_6H_5)_2]_2ZrXY$ (X = Y = CH_3, I; X = CH_3, Y = Cl, II) and

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their reactions with CO. The carbonylation reactions were performed to investigate the reactivity of the alkyl metallo ligands prior to the reactions of CO with heterobinuclear complexes, as other workers have studied the electron-deficient metal-induced migratory insertion of CO into the metal–carbon bond.[4] However, we found that the carbonylation of these metallo ligands did not lead to the observation of an acyl–zirconium complex. Instead, the reaction of CO with II gives the metallacycle $[(\eta^5\text{-C}_5\text{H}_4)\text{P}(\text{C}_6\text{H}_5)_2][(\eta^5\text{-C}_5\text{H}_4)\overline{\text{P}(\text{C}_6\text{H}_5)_2]\text{Zr}[\eta^2\text{-(OC}}\text{)CH}_3]\text{Cl}$ (III), which shows fluxional behavior in dichloromethane solution. III has been characterized by multinuclear variable-temperature NMR studies and single-crystal X-ray diffraction. The thermally unstable carbonylation product of I has been characterized by multinuclear variable-temperature NMR studies. The complexed phosphonium alkoxide fragment in III is analogous to the intermediate produced by the initial attack of a phosphite upon a carbonyl group in the Perkow reaction.[5]

Results and Discussion

The preparation of the derivative where X = Y = CH_3 (I) is accomplished by the reaction of the dichloride complex $[(\eta^5\text{-C}_5\text{H}_4)\text{P}(\text{C}_6\text{H}_5)_2]_2\text{ZrCl}_2$ with 10% excess Grignard or organolithium reagent:

$$[(\eta^5\text{-C}_5\text{H}_4)\text{P}(\text{C}_6\text{H}_5)_2]_2\text{ZrCl}_2 + 2\text{MCH}_3 \rightarrow [(\eta^5\text{-C}_5\text{H}_4)\text{P}(\text{C}_6\text{H}_5)_2]_2\text{Zr}(\text{CH}_3)_2 + 2\text{MX}$$

$$\text{M} = \text{Li, MgBr; R} = \text{CH}_3$$

The preparation of $[(\eta^5\text{-C}_5\text{H}_4)\text{P}(\text{C}_5\text{H}_5)_2]_2\text{Zr}(\text{CH}_3)\text{Cl}$ (II) is achieved by the exchange reaction with lead(II) chloride used by Wailes to prepare chloromethylzirconocene:[6]

$$[(\eta^5\text{-C}_5\text{H}_4)\text{P}(\text{C}_6\text{H}_5)_2]_2\text{Zr}(\text{CH}_3)_2 + \tfrac{1}{2}\text{PbCl}_2 \rightarrow [(\eta^5\text{-C}_5\text{H}_4)\text{P}(\text{C}_6\text{H}_5)_2]_2\text{Zr}(\text{CH}_3)\text{Cl} + \tfrac{1}{4}\text{Pb} + \tfrac{1}{4}\text{Pb}(\text{CH}_3)_4$$

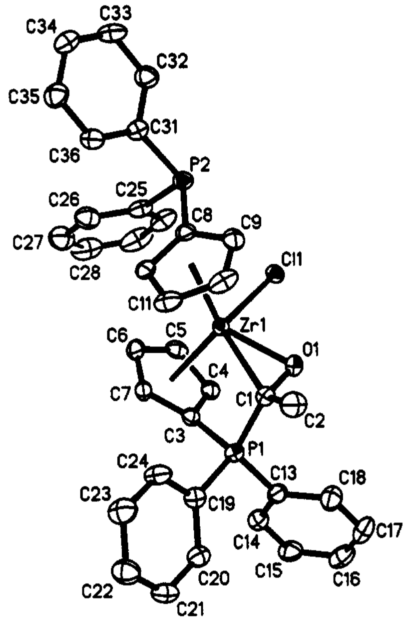

Figure 1. ORTEP diagram at the 50% probability level and atom-labeling scheme for III.

Metallo ligands I and II have been characterized by their ^{1}H and ^{31}P NMR spectra and by carbon–hydrogen analysis.

Treatment of dichloromethane solutions containing these alkyl ring-functionalized zirconocene complexes with a slight excess of CO over a 1:1 mole ratio changes the pale yellow solution to deep yellow. Peaks corresponding to the starting material in the ^{1}H NMR spectrum are absent and, at room temperature, have been replaced by broad resonances in the phenyl and cyclopentadienyl regions. No IR absorption typical of metallocene acyl complexes (1800–1600 cm^{-1}) is observed in the room-temperature infrared spectra: the difference spectra of dichloromethane solutions of I and II before and after carbonylation are featureless.

Removing the dichloromethane from the solutions obtained by the carbonylation of I and II gave yellow powders. However, the yellow solid obtained from the interaction of CO and I decomposes at room temperature over several minutes to give a brown, not yet characterized, material. The thermally stable solid obtained from the interaction of II and CO is insoluble in hydrocarbon solvents, unlike II, which is quite soluble in toluene. The powder may be recrystallized from dichloromethane/ether solutions. Although satisfactory elemental analyses were not obtained, spectroscopic data and an X-ray structure determination (vide infra) show the addition of a CO molecule to $[\text{C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2]_2\text{Zr}(\text{CH}_3)\text{Cl}$ to give $[\text{C}_5\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2][(\eta^5\text{-C}_5\text{H}_4)\overline{\text{P}(\text{C}_6\text{H}_5)_2]\text{Zr}[\eta^2\text{(OC}}\text{)CH}_3]\text{Cl}$ (III).

$$[(\eta^5\text{-C}_5\text{H}_4)\text{P}(\text{C}_6\text{H}_5)_2]_2\text{Zr}(\text{CH}_3)\text{Cl} + \text{CO} \rightarrow$$

$$\underset{\text{III}}{[(\eta^5\text{-C}_5\text{H}_4)\text{P}(\text{C}_6\text{H}_5)_2][(\eta^5\text{-C}_5\text{H}_4)\overline{\text{P}(\text{C}_6\text{H}_5)_2\text{Zr}[\eta^2\text{-(OC}}\text{)CH}_3]\text{Cl}}}$$

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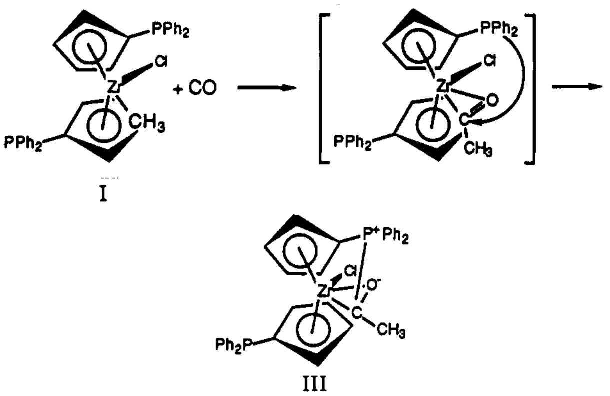
Table I. Selected Bond Distances (Å) and Bond Angles (deg) for III

bond distances				bond angles			
Zr–Cl1	2.569 (1)	Zn–Cnt1	2.260	Cl1–Zr1–O1	80.1 (1)	Cl1–Zr–C1	116.8 (1)
Zr–C1	2.299 (3)	Zr–Cnt2	2.258	C1–Zr–O1	36.8 (1)		
Zr–O1	2.065 (2)			Cnt1–Zr–Cnt2	127.4		
C1–O1	1.394 (4)			C2–C1–P1	119.2 (2)	Zr1–C1–C2	135.5 (2)
C1–C2	1.512 (5)			O1–C1–P1	110.1 (2)	O1–C1–C2	116.5 (3)
				Zr1–C1–P1	99.6 (1)	Zr1–C1–O1	62.4 (1)
P1–C1	1.782 (3)			C1–P1–C3	99.6 (1)	C8–P2–C25	103.4 (1)
P1–C3	1.779 (3)	P2–C8	1.818 (3)	C1–P1–C13	116.6 (1)	C8–P2–C31	102.7 (1)
P1–C13	1.799 (3)	P2–C25	1.843 (5)	C1–P1–C19	112.1 (1)	C25–P2–C31	100.4 (1)
P1–C19	1.806 (3)	P2–C31	1.843 (3)	C3–P1–C19	110.0 (1)		
				C3–P1–C13	108.8 (1)		
				C13–P1–C19	109.3 (1)		

Compound III decomposes in chloroform or acetone to give unidentified products. There is no apparent loss of CO from III after leaving a solid sample under a dynamic vacuum of ca. 10^{-5} mmHg for 12 h, as monitored by ^{1}H NMR spectra of samples of III before and after this treatment. Also, III is not a strong electrolyte, as indicated by ac conductivity measurements. A 1.1 mM solution of III in dichloromethane has a conductivity of 4.5 $\mu\Omega^{-1}$ compared to the conductivity of 80 $\mu\Omega^{-1}$ obtained for a 1.1 mM dichloromethane solution of $N(n\text{-}C_4H_9)_4ClO_4$.

Compound III was further characterized with use of single-crystal X-ray crystallography and variable-temperature NMR methods. The results of these studies suggest that a prompt intramolecular attack of the carbonyl carbon of an unobserved acyl intermediate by one of the phosphorus atoms bonded to the cyclopentadienyl rings occurs to give a cyclic $-Zr-C_{CO}-P-C_{Cp}-$ structure that is fluxional in solution:



Similar nucleophilic attack of CO fragments bound to metals has been previously observed by others in the study of reactivity of metal complexes with amphoteric ligands leading to the formation of "acyl–phosphonium ions"[7] as well as work with phosphinomethyl zirconocene complexes in which intramolecular[8a] and intermolecular[8b,c] attack of phosphorus upon the carbonyl carbon have been observed.

X-ray Molecular Structure of $[(\eta^5\text{-}C_5H_4)P(C_6H_5)_2][(\eta^5\text{-}C_5H_4)\overline{P(C_6H_5)_2]Zr}[\eta^2\text{-}(OC)CH_3]Cl$. The structure of the carbonylation product was determined by single-crystal X-ray diffraction methods; an ORTEP diagram is shown in Figure 1, and selected bond distances and angles can be found in Table I. The zirconium atom is bonded to two η^5-C_5H_4 rings, the chlorine atom, and the carbon and oxygen atoms of the CO, which has inserted into the Zr–CH_3 bond. The C–O fragment is oriented in the O-inside conformation observed in other group 4 metallocene acyl complexes. In this complex, however, a phosphorus atom from one of the diphenylphosphino groups is bonded to the carbon derived from the CO.

The two η^5-cyclopentadienide ligands are bound to the zirconium atom with slightly longer Zr–C bond lengths (Zr1–Cnt = 2.26 Å average) than other zirconocene fragments (ca. 2.22–2.23 Å).[9,10] There are three other atoms bound to the zirconium atom: the chlorine and the carbon and oxygen of the inserted CO. The Zr–Cl1 bond distance is quite long: 2.569 (1) Å compared to 2.41 Å (average) in the complex $[(\eta^5\text{-}C_5H_4)P(C_6H_5)_2]_2ZrCl_2\cdot Mo(CO)_4$,[1] which contains the complexed metallo ligand, and 2.45 Å in the Zr–Cl bond of (μ-oxo)bis[chlorodicyclopentadienylzirconium(IV)].[9] The Zr1–O1 bond at 2.065 (2) Å is longer than the Zr–O bonds in most zirconocene complexes (1.94–1.96 Å)[10] but still shorter than the 2.15–2.20 Å expected for a Zr–O single bond.[11] This bond length is considerably shorter than that observed in $Cp_2Zr[\eta^2(C{=}O)CH_3](CH_3)$, where the Zr–O distance is 2.290 Å.[12] These results suggest that a Zr–O single bond is present in this complex, but less O pπ → Zr dπ back-bonding occurs because of the other two donor atoms, C and Cl. However, the Zr–O bond in III appears stronger than that in the "traditional" zirconocene acyl complexes, as judged by the criterion of bond length. The Zr–C1 distance is 2.299 (3) Å. This bond is larger than the Zr–C(acyl) bond in the zirconocene acyl formed by the reaction of CO and dimethyl zirconocene (2.197 Å)[12] and slightly longer than dialkyl zirconocenes, which have Zr–C(alkyl) bonds of ca. 2.24 Å[13] and the 2.276 Å Zr–C(methyl) bond in (μ-oxo)-bis[methyldicyclopentadienylzirconium(IV)].[14]

The geometry about the carbon derived from carbon monoxide is a distorted tetrahedron, where distortion arises from the η^2 binding of the C–O unit and the four-membered -Zr–C–P1–C1- ring. This distortion results in the Zr1–C1–O1 angle of 62.4 (1)°, 16° smaller than that

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in $Cp_2Zr[(C{=}O)CH_3](CH_3)$. The four-membered –Zr–C–P1–C1– ring is probably responsible for the Zr1–C1–P1 angle of 99.6 (1)°, about 10° smaller than the ideal tetrahedral angle. The bond distances about the carbon atom are consistent with single bonds to the other atoms. The C1–O1 distance of 1.394 (4) Å is in the range for a C–O single bond, and the C1–C2 (1.512 (5) Å) distance is typical for C–C single bonds.

The two phosphorus atoms show very different coordination geometries. P1, bonded to the carbonyl carbon, is nearly tetrahedrally coordinated with most angles near the ideal tetrahedral angle, the exception being the angle of 99.6 (1)° in the cyclic unit C1–P1–C3, which is 10° smaller than the ideal value. P2 is trigonal pyramidal with nearly equal bond angles of about 100°. The bond distances about the two phosphorus atoms are distinctly different; those about P1 are shorter (1.79–1.81 Å) and are consistent with those observed in phosphonium salts,[15] and those about P2 (1.83–1.86 Å) are similar to those observed in triphenylphosphine[16] and uncoordinated ferrocenylphosphines.[17] The P1–C1 bond length is too long to be that of an ylide: a P=C bond distance would be expected to be about 1.6–1.7 Å,[18] whereas the bond lengths and angles about P1 in III are in accord with a four-coordinate phosphonium formulation.[18,19]

On the basis of these bond lengths, the complex may be described as a zirconocene containing an acyl–phosphonium ion with a phosphonium cation and a coordinated alkoxide anion. The result is an 18-electron complex, since the chloride, oxygen, and carbon atoms are 2-electron donors and the two η^5-C_5H_4 rings each provide 6 electrons to the d^0 Zr(IV) center. The longer bond lengths in this complex are consistent with the results from Lauher and Hoffmann's work, which predicts that filling of the metal-based LUMO (through the alkoxide oxygen atom in this case) will result in lengthening of the remaining metal–ligand bonds compared to those in 16-electron Cp_2ML_2 complexes.[20] The triple bond in the CO has been reduced to a single bond in the alkoxide through insertion into the Zr–C bond and the oxidation of the phosphorus ligand to a phosphonium center. The Zr–O, Zr–Cl, and Zr–Cnt distances are similar to those found in tris[(η^2-formaldehyde)zirconocene], where the oxygen atom of each formaldehyde unit bridges two zirconium atoms to give a six-membered ring[21] ($Zr{-}C_{average}$ = 2.27 Å, $Zr{-}O_{average}$ = 2.16 Å, and $Zr{-}Cnt_{average}$ = 2.26 Å). The slightly longer Zr–O distances observed in this trimeric complex likely result from the bridging mode adopted by the oxygen atoms. The longer bond distances observed in the trimer and compound III probably illustrate the effect of the zirconium atom achieving an 18-electron configuration.

Carbonylation of the phosphinomethyl zirconocene complexes $(\eta^5$-$C_5H_5)_2ZrCl(CH_2PR_2)$ (R = CH_3,[8c] C_6H_5[8b]) leads to binuclear complexes, $[(\eta^5$-$C_5H_5)_2ZrCl]_2(\mu$-$PR_2CH{=}CO)$, containing coordinated ketene with the oxygen atom bridging the two Zr atoms. The coordination sphere of one of the zirconium atoms is similar to that of III: two η^5-cyclopentadienyl rings, a chloride ligand, and the carbon and oxygen atoms derived from inserted CO. The Zr–C distances in these complexes are slightly shorter than in III, 2.23 (2) and 2.231 (9) Å (R = CH_3 and C_6H_5, respectively), but the Zr–O distances are longer, 2.26 (1) Å (R = CH_3) and 2.278 (7) Å (R = C_6H_5), presumably due to the bridging mode in the binuclear complexes. The Zr–Cl distances are quite similar, 2.561 and 2.563 Å (R = CH_3 and C_6H_5, respectively) compared to 2.569 Å in III. The C–O distances in these complexes are significantly shorter, 1.35 (2) and 1.330 (16) Å (R = CH_3 and C_6H_5, respectively) than in III, consistent with the alkoxide formulation of III. These ketene complexes result from the abstraction of a hydrogen atom of the acyl group by a phosphinomethyl group on another zirconocene complex.[8b,c] In contrast, III undergoes an intramolecular attack by the ring-bound phosphine group, which results in reduction of the acyl to a coordinated alkoxide. The NMR studies described below show that the phosphine attack in III is reversible, unlike that occurring in the phosphinomethyl complexes.

NMR Studies. The room-temperature ^1H NMR spectrum of III in dichloromethane-d_2 shows broad peaks in the phenyl region (δ 7.6) and cyclopentadienide region (δ 6.4, 6.05, 5.91, 5.7) and a sharp triplet at δ 2.01 (J_{P-H} = 8.4 Hz). Cooling the sample to −80 °C results in the sharpening of all the lines.[22] (A stacked plot of the variable-temperature NMR results is shown in Figure 2.) However, the triplet found at δ 2.01 and 298 K is now a doublet, δ 1.96 (J_{P-H} = 16.7 Hz). Use of enriched ^{13}CO resulted in the splitting of all the lines of the methyl resonance into doublets (J_{C-H} = 5.4 Hz at 193 and 294 K). The cyclopentadienyl signals broadened and coalesced to give four signals at temperatures above 5 °C, and a limiting spectrum was obtained at 30 °C. Line-shape analysis of these spectra give an activation enthalpy of 61 ± 5 kJ/mol and an activation entropy of about 24 ± 15 J/(mol K).

The variable-temperature $^{31}P\{^1H\}$ NMR study showed two broad resonances centered at about δ −15 and 10 at 294 K. Cooling to 193 K sharpens these lines, and two sharp resonances are observed at δ −21.34 and 11.68. The upfield peak is quite close to the resonance observed for the free metallo ligand, and the downfield resonance's chemical shift is similar to that observed for alkyl phosphonium salts.[23] Use of enriched ^{13}CO splits the resonance at δ 11.68 into a doublet (J_{P-C} = 38.0 Hz). This coupling constant is considerably smaller than those observed in ylides (80–110 Hz)[24] but only slightly larger than those observed in a variety of phosphonium salts.[25] A fast exchange limiting $^{31}P\{^1H\}$ spectrum could not be obtained in dichloromethane. The room-temperature $^{13}C\{^1H\}$ spectrum (with ^{13}CO) shows a broad peak at about δ 59. When the compound is cooled to 193 K, the broad resonance shifts upfield and sharpens to give a doublet at δ 52.00 (J_{P-C} = 37.9 Hz). The chemical shifts of the carbon atoms involved are consistent with the phosphonium salt description (δ(^{13}C) 34–40).[26] The lower chemical shift of

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[22] ^1H NMR at 203 K: phenyl region, δ 7.72 (m) 7.62 (m), 7.32 (m); cyclopentadienide region, δ 6.50 (m, 1 H); δ 6.24 (m, 1 H); δ 6.13 (m, 1 H); δ 6.09 (m, 1 H); δ 6.01 (m, 1 H); δ 5.91 (m, 1 H); δ 5.77 (m, 1 H), 5.41 (m, 1 H). ^1H NMR at 326 K: cyclopentadienide region, δ 5.793 (m, 2 H), 5.986 (m, 2 H), 6.101 (m, 2 H), 6.346 (m, 2 H).

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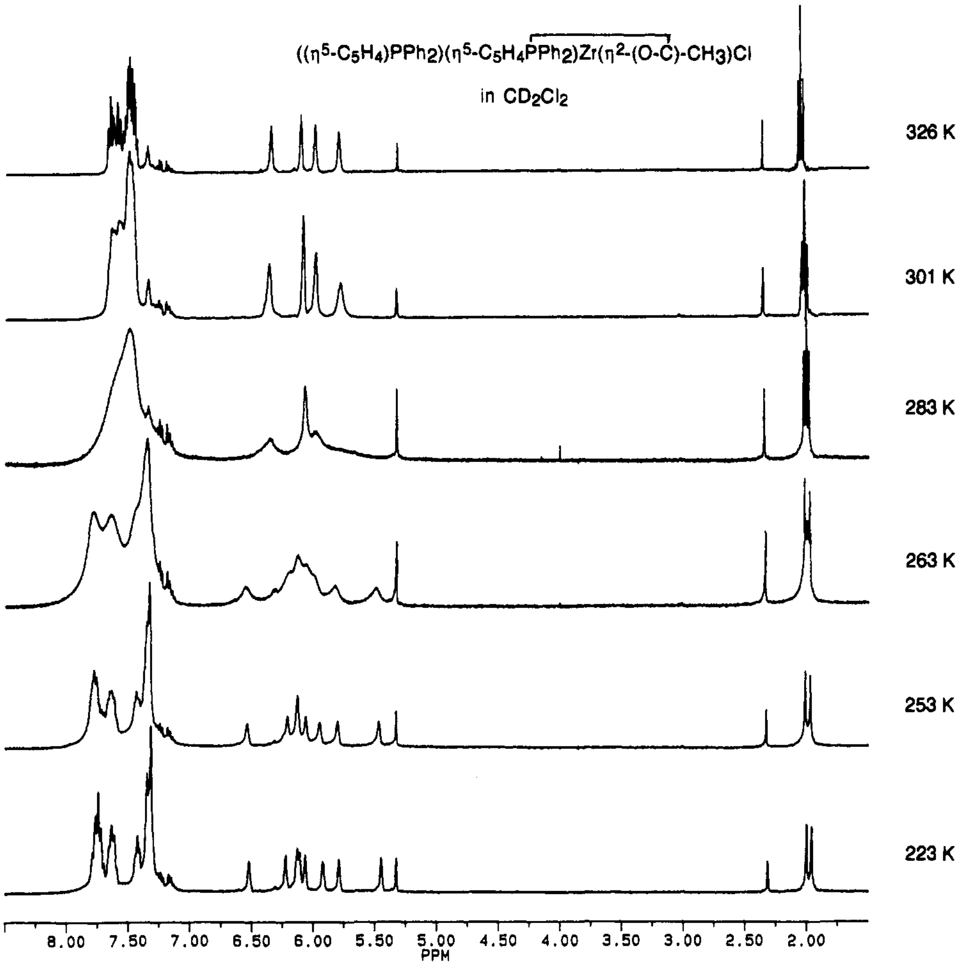


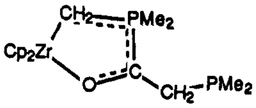
Figure 2. Stacked plot of the variable-temperature ^1H NMR spectra of $[(\eta^5\text{-}C_5H_4)P(C_6H_5)][(\eta^5\text{-}C_5H_4)P(C_6H_5)]ZrCl(OCCH_3)$ in methylene chloride-d_2.

the carbon atom derived from CO (δ 52) in III compared to that of α-carbon atoms in other phosphonium salts may arise from an inductive effect, since the carbon atom is bonded to an oxygen atom.

A possible mechanism for the dynamic process invokes intramolecular attack of C1 by the phosphorus(III) center. Either a dissociative (S_N1 type) mechanism, where P1 first dissociates, or an associative/interchange (S_N2 type) mechanism, where P2 displaces P1, could be active as shown in Scheme I. The newly formed phosphine (P1) is now free to attack the "acyl" carbon in the same fashion. Of the two mechanisms suggested for the fluxional behavior in Scheme I, the interchange route is favored because there is no sign of a free acyl at low temperatures in the NMR spectra or at ambient temperatures in the IR spectra.

Similar results are observed in the variable-temperature NMR studies of the carbonylation of the dimethyl complex I with 1 mol of CO/mol of I, although this carbonylation product is much less stable than III. Solution studies at room temperature in sealed NMR tubes show a multiplet at δ 2.01 and a broad singlet at δ −0.317 of equal areas corresponding to the two methyl groups; broad resonances are observed in the cyclopentadienyl and phenyl regions. Cooling the solution leads to sharpening of all the resonances in the NMR spectra. At 203 K, the proton spectrum shows the methyl peaks as a doublet of doublets at δ 1.81 ($J_{\text{P-C}}$ = 17.1 Hz, $J_{\text{C-H}}$ = 5.2 Hz) and a singlet at δ −1.18 of equal area. The cyclopentadienyl region shows seven resonances,[27] and the phenyl resonances are a complex group of overlapping multiplets. The room-temperature $^{31}P\{^1H\}$ NMR spectrum shows two broad resonances at about δ 10 and −15. At 203 K with ^{13}C-enriched CO, the $^{31}P\{^1H\}$ spectrum shows two sharp resonances, a doublet at δ 12.8 ($J_{\text{P-C}}$ = 40 Hz) and a singlet at δ −19.4. The $^{13}C\{^1H\}$ spectrum at 203 K shows a doublet at δ 38.71 ($J_{\text{C-P}}$ = 42 Hz). The general similarities in the spectral data suggest that a process similar to that occurring in III is operative in this compound as well. The process is further complicated by the second methyl group, which may participate if the CO scrambles between the two methyl groups.

This attack of the carbonyl carbon by phosphorus is similar to that proposed in the carbonylation of bis[(dimethylphosphino)methyl] zirconocene reported by Karsch et al.,[11a] giving B, which is also fluxional.



B

However, B is different from III in at least two ways. The fluxional process does not involve a reversible ex-

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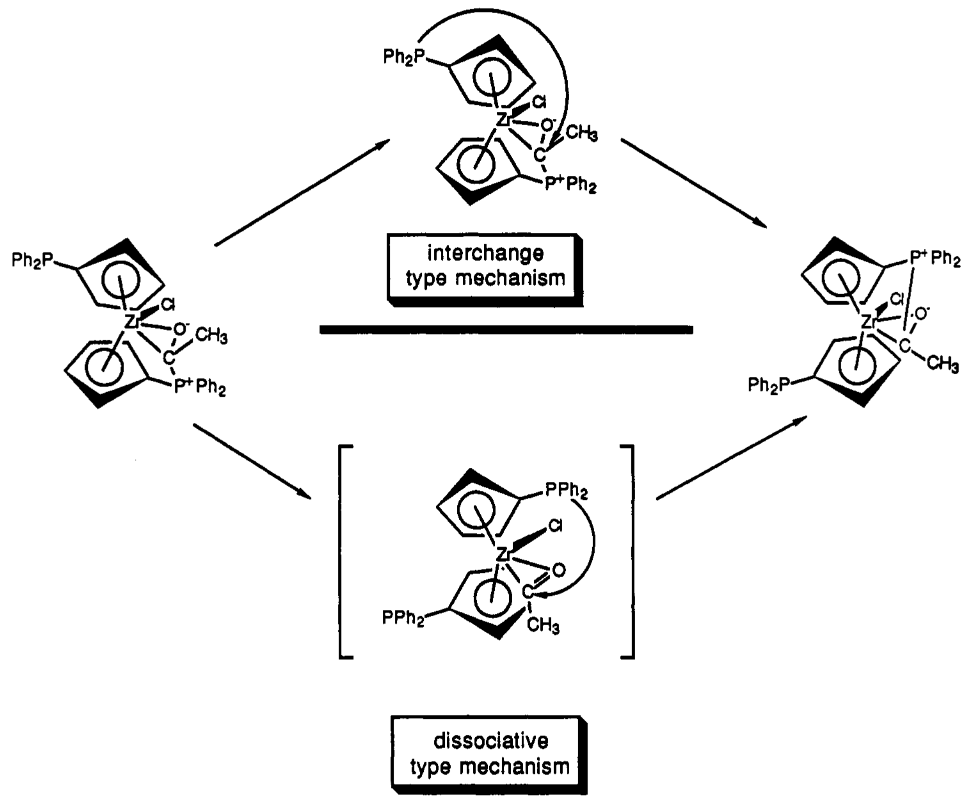
(26) Abell, A. D.; Trent, J. O.; Whittington, B. I. *J. Org. Chem.* **1989**, *54*, 2762 and references therein.

(27) ^1H NMR for cyclopentadienyl region: at 203 K δ 6.1893 (1 H), 6.1454 (1 H), 6.0637 (2 H), 5.999 (1 H), 5.800 (1 H), 5.517 (1 H), 5.0535 (1 H): at 318 K, δ 5.85105 (2 H), 5.7339 (2 H), 5.6867 (2 H), 5.5884 (2 H).

Scheme I



change of the phosphorus atoms at the carbon derived from CO due to the rearrangement upon attack of the carbonyl carbon. Also, the phosphorus–carbon coupling constant ${}^1J_{P-C}$ = 83.0 Hz in B is much larger than in the carbonylation products of I and II. This latter point is consistent with the higher bond order of the P–C bond assigned in B.

A common feature between the two complexes in the initial formation of the acyl where the carbonyl carbon is susceptible to attack. This enhanced reactivity of the carbonyl group can be attributed to the "carbenoid" character of the postulated acyl intermediate, as described by Tatsumi et al.[28] In d^0 acyl zirconocene complexes, the π^* CO orbitals are low in energy and are properly oriented (normal to the plane defined by Zr, C, and O) for attack by the phosphine nucleophile of a ring-functionalized metallocene.

Further studies are directed toward characterizing the products of carbonylation of I and other alkyl derivatives of ring-functionalized zirconocenes and the reactivity of these carbonylation products toward external nucleophiles. We are also pursuing the preparation of heterobinuclear complexes of these metallo ligands with platinum-group metals and investigating their reactions with CO and other small molecules.

Table II. Experimental Data for the X-ray Diffraction Study

formula: $C_{36}H_{31}OP_2ClZr$
fw: 668.2
temp (K): 183
cryst syst: monoclinic
space group: $P2_1/c$ (C_{2h}^5; No. 14)
a = 12.3056 (12) Å
b = 18.5738 (18) Å
c = 13.5718 (15) Å
β = 101.285 (8)°
V = 3042.0 (5) Å^3
Z = 4
D_{calcd} = 1.459 g cm^{-3}
diffractometer: Syntex P2$_1$ (R3m/V system)
radiation: Mo Kα (λ = 0.710730 Å)
monochromator: highly oriented graphite
data collected: $+h,+k,\pm l$
scan type: coupled θ(crystal)–2θ(counter)
scan width: symmetrical, 1.2° plus Kα separation
scan speed: fixed, 3.0 deg min^{-1} (in ω)
2θ range: 4.0–50.0°
μ(Mo Kα) = 0.574 mm^{-1}
abs cor: semiempirical (ψ-scan method)
no. of rflns collected: 5874
no rflns with $|F_o| > 2.0\sigma(|F_o|)$: 4851
no. of variables: 495
R_F = 3.6%, R_{wF} = 4.3%
goodness of fit: 1.49

Experimental Section

General Considerations. Most of the compounds described are air sensitive and were prepared with use of either Schlenk or high-vacuum techniques. Solid compounds were manipulated in a Vacuum Atmospheres Corp. (VAC) HE-43 Dri-Lab with an HE-63P Pedatrol pressure regulator and HE-393 Dri Train. The inert gas used in the glovebox and Schlenk and vacuum lines is either nitrogen or argon, which is further purified by passage through activated Chemalog R3-11 catalyst and activated 4A molecules sieves. Solvents were all reagent grade and were further purified by standard techniques. $[(C_5H_4P(C_6H_5)_2]_2ZrCl_2$ was prepared as previously described.[1]

Physical Measurements. ^1H and ^{31}P NMR spectra were obtained with a Bruker AM-400 spectrometer. Proton NMR spectra were referenced by either the residual proton resonance or internal TMS; ^{31}P NMR spectra were referenced against external $P(OCH_3)_3$. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, NY.

$[(\eta^5\text{-}C_5H_4)P(C_6H_5)_2]_2Zr(CH_3)_2$ (I). A 50-mL Schlenk flask is loaded with $[(C_5H_4P(C_6H_5)_2]_2ZrCl_2$ (1.00 g, 1.51 mmol), and 30 mL of toluene is added to produce a yellow solution. This solution is cooled to −77 °C, and 1.1 mL of 3.0 M CH_3MgBr in diethyl ether

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[28] Tatsumi, K.; Nakamura, A.; Hofmann, P.; Stauffert, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1985**, *107*, 4440.

Table III. Atomic Coordinates ($\times10^4$; $\times10^3$ for H) and Equivalent Isotropic Displacement Coefficients (Å^2 $\times$ 10^4; Å^2 $\times$ 10^3 for H) for III

	x	*y*	*z*	*U*(eq)^a		*x*	*y*	*z*	*U*(eq)^a
Zr1	1305.2 (0.2)	2299.3 (0.1)	4889.2 (0.2)	181 (1)	C32	5156 (3)	-13 (2)	6712 (3)	324 (11)
Cl1	2159.6 (0.6)	1749.5 (0.4)	3478.3 (0.5)	221 (2)	C33	5744 (3)	-378 (2)	7543 (3)	385 (12)
P1	-533.4 (0.6)	3491.7 (0.4)	4514.2 (0.6)	222 (2)	C34	5631 (3)	-172 (2)	8484 (3)	340 (11)
P2	3801.7 (0.6)	1011.0 (0.4)	5652.4 (0.6)	239 (2)	C35	4935 (3)	379 (2)	8618 (3)	337 (11)
O1	-79 (2)	2262 (1)	3751 (2)	255 (7)	C36	4335 (3)	732 (2)	7790 (2)	290 (10)
C1	-565 (2)	2532 (2)	4521 (2)	242 (9)	H2A	-230 (3)	225 (2)	412 (3)	39 (10)
C2	-1597 (3)	2152 (2)	4697 (3)	353 (12)	H2B	-145 (3)	164 (2)	474 (3)	48 (11)
C3	925 (2)	3631 (2)	4801 (2)	213 (9)	H2C	-175 (3)	229 (2)	527 (3)	40 (11)
C4	1596 (3)	3502 (2)	4088 (2)	235 (9)	H4A	135 (3)	352 (2)	341 (2)	21 (8)
C5	2655 (3)	3312 (2)	4611 (3)	262 (10)	H5A	323 (3)	322 (2)	436 (2)	30 (9)
C6	2651 (3)	3330 (2)	5638 (3)	293 (10)	H6A	318 (3)	324 (2)	612 (3)	28 (9)
C7	1588 (3)	3512 (2)	5772 (2)	238 (9)	H7A	136 (3)	352 (2)	634 (2)	22 (8)
C8	2502 (2)	1331 (2)	5938 (2)	219 (9)	H9A	137 (3)	64 (2)	507 (3)	37 (10)
C9	1475 (3)	994 (2)	5516 (2)	281 (10)	H10A	-6 (3)	122 (2)	579 (3)	35 (10)
C10	642 (3)	1304 (2)	5935 (3)	339 (11)	H11A	71 (3)	218 (2)	698 (3)	35 (9)
C11	1109 (3)	1851 (2)	6596 (2)	332 (11)	H12A	277 (3)	214 (2)	701 (2)	29 (9)
C12	2250 (3)	1855 (2)	6625 (2)	253 (10)	H14A	-12 (3)	481 (2)	354 (3)	46 (11)
C13	-1090 (2)	3925 (2)	3339 (2)	255 (9)	H15A	-99 (3)	534 (2)	206 (3)	36 (10)
C14	-732 (3)	4600 92)	3101 (2)	304 (10)	H16A	-239 (3)	482 (2)	100 (3)	39 (10)
C15	-1228 (3)	4932 (2)	2210 (3)	343 (11)	H17A	-298 (3)	367 (2)	131 (3)	47 (11)
C16	-2069 (3)	4585 (2)	1562 (3)	383 (12)	H18A	-204 (3)	314 (2)	282 (2)	21 (8)
C17	-2405 (3)	3905 (2)	1775 (3)	387 (12)	H20A	-206 (3)	468 (2)	460 (3)	29 (8)
C18	-1922 (3)	3575 (2)	2666 (3)	333 (11)	H21A	-279 (3)	518 (2)	585 (2)	31 (9)
C19	-1164 (2)	3874 (2)	5489 (2)	245 (9)	H22A	-244 (3)	474 (2)	757 (3)	47 (10)
C20	-1868 (3)	4467 (2)	5276 92)	264 (10)	H23A	-116 (3)	375 92)	783 (3)	47 (11)
C21	-2313 (3)	4770 (2)	6037 (3)	313 (11)	H24A	-53 (3)	319 (2)	663 (2)	28 (9)
C22	-2068 (3)	4495 (2)	7003 (3)	366 (12)	H26A	486 (3)	202 (2)	721 (3)	47 (11)
C23	-1373 (3)	3905 (2)	7209 (3)	370 (12)	H27A	591 (3)	306 (2)	715 (3)	41 (11)
C24	-929 (3)	3594 (2)	6456 (3)	326 (11)	H28A	636 (4)	350 (2)	574 (3)	70 (14)
C25	4659 (3)	1831 (2)	5739 (2)	290 (10)	H29A	574 (3)	290 (2)	420 (3)	56 (12)
C26	5068 (3)	2209 (2)	6621 (3)	366 (12)	H30A	468 (3)	183 (2)	425 (3)	35 (10)
C27	5702 (3)	2816 (2)	6607 (3)	462 (14)	H32A	526 (3)	-14 (2)	610 (3)	33 (9)
C28	5951 (3)	3063 (2)	5715 (4)	502 (15)	H33A	621 (3)	-77 (2)	749 (3)	49 (11)
C29	5575 (3)	2691 (2)	4838 (3)	495 (15)	H34A	603 (3)	-40 (2)	906 (3)	55 (12)
C30	4931 (3)	2080 (2)	4846 (3)	393 (12)	H35A	483 (3)	54 (2)	933 (3)	52 (11)
C31	4453 (2)	552 (2)	6823 (2)	244 (9)	H36A	382 (3)	113 92)	784 (13)	37 (10)

^{a} Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

(3.30 mmol, 10% excess) is added dropwise by syringe. The solution is removed from the cold bath and stirred at room temperature for 0.5 h, at which point gentle heating is started. After the mixture is heated for 0.5 h, a tan solution with a white suspended solid results. The solvent is removed in vacuo to give an off-white solid, which is washed three times with 5-mL aliquots of pentane and then dried in vacuo. The crude product and salt is then transferred to an extractor. After a 10-h extraction with refluxing heptane, the solvent is removed from the filtrate suspension. The white, powdery, analytically pure product results (0.71 g) in 76% yield based on $[(C_5H_4P(C_6H_5)_2]_2ZrCl_2$. Alternatively, one can recrystallize the product by layering a toluene solution with hexane. NMR (in C_6D_6): ^{1}H δ 7.41 (m, 8 H, aromatics), 7.00 (m, 12 H, aromatics), 5.93 (s, 8 H, cyclopentadienide), 0.016 (s, 6 H, methyl); ^{31}P, −18.7 (s). Anal. Calcd (found) for $C_{36}H_{34}P_2Zr$: C, 69.76 (68.99); H, 5.53 (5.54).

$[(\eta^5\text{-}C_5H_4)P(C_6H_5)_2]_2Zr(CH_3)Cl$ (II). A 50-mL Schlenk flask is loaded with 457 mg of $[(C_5H_4P(C_6H_5)_2]_2Zr(CH_3)_2$ (737 μmol), 100 mg of $PbCl_2$ (360 μmol), and a magnetic stirring bar. About 10 mL of toluene is added to the solids, and the suspension is stirred at room temperature for 3 days to give a black suspension, which settles slowly to reveal a yellow solution and a black precipitate (presumably metallic lead). The suspension is filtered to give a clear yellow solution, and the filter cake is washed two times with 1-mL portions of toluene. The solvent is removed in vacuo to give an oily pale yellow product. Trituration of this product with about 3 mL of hexane for 3 h results in a white suspension. Filtering and subsequent washing of the filter cake with hexane followed by drying in vacuo gives 0.362 g of product as a white powder in ca. 98% purity (77% based on I). Analytically pure material is difficult to obtain, as starting material co-crystallizes with III. Repeated crystallization of III from toluene layered with pentane gives analytically and spectroscopically pure III. NMR (in C_6D_6): ^{1}H δ 7.40 (m, 8 H, aromatics), 7.01 (m, 12 H, aromatics), 6.07 (m, 4 H, cyclopentadienide), 5.98 (m, 4 H, cyclopentadienide), 5.85 (m, 2 H, cyclopentadienide), 0.589 (s, 3 H, methyl); ^{31}P, δ −18.3. Anal. Calcd (found) for $C_{35}H_{31}P_2ClZr$: C, 65.66 (65.74); H, 4.88 (5.03).

$[(\eta^5\text{-}C_5H_4)P(C_6H_5)_2][(\eta^5\text{-}C_5H_4)\overline{P(C_6H_5)_2]Zr[\eta^2\text{-}(OC}CH_3]Cl$ (III). A sample (0.256 g, 0.400 mmol) of $[(\eta^5\text{-}C_5H_4)PPh_2]_2Zr(CH_3)Cl$ was loaded into a 10-mL pear-shaped flask, which was fitted to a rotating frit assembly. This unit was mounted onto the vacuum line, and 3 mL of dichloromethane was vacuum-distilled onto the solid. After it was warmed to room temperature, the solution was filtered and the frit washed three times with 1-mL portions of back-distilled dichloromethane. The clear, pale yellow solution was then exposed to 0.5 atm of CO (CP grade) and stirred for 4 h, during which time the solution turned orange. The solvent was then removed under vacuum and the orange/yellow residue washed with 2 mL of toluene and two 3-mL portions of hexane. The resulting yellow powder was dried in vacuo for 6 h. A yield of 0.230 g (0.344 mmol) was obtained, or 86.1% based on starting metallo ligand. III could also be recrystallized from dichloromethane solutions layered with diethyl ether. Anal. Calcd (found) for $[C_5H_4P(C_6H_5)_2]_2Zr(COCH_3)Cl$: C, 64.70 (62.42); H 4.68 (4.91).

X-ray Structure Determination of III. A light yellow crystal of approximate dimensions 0.33 × 0.40 × 0.40 mm was oil-mounted on a glass fiber and transferred to a Syntex P21 diffractometer equipped with a locally modified LT-1 low-temperature system. The determination of Laue symmetry, crystal class, unit cell parameters, and the crystal orientation matrix was carried out by previously described methods, similar to those of Churchill.[29] Intensity data were collected at 183 K with use of the θ–2θ scan technique under the conditions listed in Table II. All 5874 data were corrected for absorption by application of a semiempirical (ψ-scan, μ(Mo Kα) = 0.574 mm^{-1}) method and for Lorentz and

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(29) Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J. *Inorg. Chem.* 1977, *16*, 265.

polarization effects and placed on an approximately absolute scale. The diffraction symmetry was $2/m$ with systematic absences $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$. The space group is therefore uniquely defined as the centrosymmetric monoclinic $P2_1/c$ (C^5_{2h}; No. 14).

All crystallographic calculations were carried out with use of either the UCI modified version of the UCLA Crystallographic Computing Package[30] or the SHELXTL PLUS program set.[31] The analytical scattering factors for neutral atoms were used throughout the analysis;[32a] both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion[32b] were included. The quantity minimized during least-squares analysis was $\sum w(|F_o| - |F_c|)^2$, where $w^{-1} = \sigma^2(|F_o|) + 0.004(|F_o|)^2$. The structure was solved by an automatic Patterson routine (SHELXTL PLUS) and refined by full-matrix least-squares techniques. Hydrogen atoms were located from subsequent difference-Fourier syntheses and included with isotropic temperature factors. Refinement of positional and thermal parameters led to convergence with $R_F = 3.6\%$, $R_{wF} = 4.3\%$, and GOF = 1.49 for 495 variables refined against those 4851 data with $|F_o| > 2.0\sigma(|F_o|)$ ($R_F = 2.9\%$ and $R_{wF} = 4.2\%$ against those 4314 data with $|F_o| > 6.0\sigma(|F_o|)$). A final difference-Fourier synthesis showed no significant features; $\rho(\max) = 0.67$ e Å^{-3}. The atomic positions are given in Table III.

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Supplementary Material Available: Tables of experimental data, thermal parameters, and bond distances and angles (7 pages); a table of structure factor amplitudes (19 pages). Ordering information is given on any current masthead page.

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